Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information

Pressure-Induced Ge_2Se_3 and Ge_3Se_4 Crystals with Low Superconducting Transition Temperatures

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The superconducting transition temperature was predicted using the Allen-Dynes modified McMillan's equation [1, 2]:

$$T_c = \frac{\omega_{log}}{1.2} exp[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}]$$

where ω_{log}, μ^*, and λ are the logarithmic average frequency, the Coulomb pseudopotential, and the total EPC parameter. ω_{log} and λ were estimated based on the Eliashberg phonon spectral function $\alpha^2F(\omega)$:

$$\lambda = 2\int_0^\infty \frac{\alpha^2F(\omega)}{\omega} d\omega$$

$$\omega_{log} = exp[\frac{2}{\lambda}\int_0^\omega \frac{\alpha^2F(\omega)log\omega}{\omega} d\omega]$$

A kinetic energy cut-off of 40 Ry was applied in all EPC calculations. To obtain the value of λ, a smearing value of 0.12 was used. Typical values of μ^* in between 0.1 and 0.14 were used in evaluating the T_c.

TABLE S1. Superconducting transition temperatures T_c of different Ge_2Se_3 and Ge_3Se_4 phases under pressures.

Compounds	Pressures (GPa)	Space groups	μ^*	T_c (K)
Ge_2Se_3	5	$R3m$	0.1	1.35
			0.14	0.57
Ge_2Se_3	10	$P\bar{3}m1$	0.1	1.92
			0.14	0.96
Ge_2Se_3	15	$R\bar{3}m$	0.1	1.98
			0.14	0.98
Ge_3Se_4	40	$I\bar{4}3d$	0.1	4.50
			0.14	2.83
Amorphous Ge_2Se_3 [3]	>20	-	-	∼2

TABLE S2. Space groups, lattice constants, and Wyckoff positions of different Ge-Se compounds and phases at selected pressures.

Compounds	Pressures (GPa)	Space groups	Lattice paramters	Wyckoff positions
Ge_2Se_3	5	$R3m$	$a = 3.660$Å $c = 27.342$Å	Ge 3a (0,0,0.162) Ge 3a (0,0,0.293) Se 3a (0,0,0.776) Se 3a (0,0,0.561) Se 3a (0,0,0.011)
Ge_2Se_3	10	$P\bar{3}m1$	$a = 3.637$Å $c = 8.598$Å	Ge 2d (0.333,0.667,0.806) Se 2d (0.333,0.667,0.360) Se 1a (0,0,0)
Ge_2Se_3	15	$R\bar{3}m$	$a = 3.586$Å $c = 25.180$Å	Ge 6c (0,0,0.399) Se 3a (0,0,0) Se 6c (0,0,0.789)
Ge_3Se_4	40	$I\bar{4}3d$	$a = 7.547$Å	Ge 12a (0.375,0,0.25) Se 16c (0.069,0.069,0.069)

TABLE S3. The shortest bond lengths L and the mean coordination numbers $\bar{n}$ in Ge_2Se_3 and Ge_3Se_4. $\bar{n}_{\alpha-\beta}$ is the the mean number of nearest neighbors of β atoms around an α atom within a distance of 2.9 Å [4]. Amorphous data were reported at ambient conditions.

	Phases	L_{Ge-Se} (Å)	L_{Ge-Ge} (Å)	L_{Se-Se} (Å)	$\bar{n}_{Ge-Se}$	$\bar{n}_{Ge-Ge}$	$\bar{n}_{Se-Se}$
Ge_2Se_3	$R3m$ 5GPa	2.55	3.57	3.43	3	0	0
	$P\bar{3}m1$ 10GPa	2.54	3.64	3.19	6	0	0
	$R\bar{3}m$ 15 GPa	2.65	3.59	3.03	6	0	0
	Amorphous [4]	2.35	2.47	2.37	3.21	0.52	0.01
Ge_3Se_4	$I\bar{4}3d$ 40GPa	2.50	3.53	2.92	8	0	0
	Amorphous [5]	2.35	2.48	-	2.73	1.37	-

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